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K. Balasubramanian

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Non-rigid Group Theory, Tunneling Splittings and Nuclear Spin Statistics of Water Pentamer: (H₂O)₅

K. Balasubramanian^{*}

*Center for Image Processing and Integrated computing, University of
California Davis, Livermore, CA 94550; University of California
Chemistry and Material Science Directorate
Lawrence Livermore National Laboratory
Livermore, California 94550;
and Glenn T Seaborg Center, Lawrence Berkeley Laboratory, University
of California, Berkeley, CA 94720*

The character table of the fully non-rigid water pentamer, (H₂O)₅ is derived for the first time. The group of all feasible permutations is the wreath product group S₅[S₂] and it consists of 3840 operations divided into 36 conjugacy classes and irreducible representations. We have shown that the full character table can be constructed using elegant matrix type generator algebra. The character table has been applied to the water pentamer by obtaining the nuclear spin statistical weights of the rovibronic levels and tunneling splittings of the fully non-rigid pentamer. We have also obtained the statistical weights and tunneling splittings of a semi-rigid deuterated pentamer that exhibits pseudo rotation with an averaged C_{5h}(G₁₀) symmetry used in the assignment of vibration-rotation-tunneling spectra. The correlation tables have been constructed for the semi-rigid (G₁₀) to non-rigid (G₃₈₄₀) groups for the rotational levels and tunneling levels. The nuclear spin statistical weights have also been derived for both the limits.

^{*} Address correspondence at kbala@ucdavis.edu or fax:925-422-6810

1. Introduction

Laser spectroscopy and dynamics of water clusters have been the topic of numerous studies for many years.¹⁻¹² Water clusters are particularly intriguing due to the interplay of hydrogen bonding and floppy motions that result in novel quantum tunneling dynamics.¹⁻¹⁵ Some of the water clusters also exhibit chirality in their equilibrium geometries and thus quantum tunneling among chiral isomers has received attention.^{11,2,3} One of the reasons for so much activity and interest in studying water clusters is that such studies could provide significant insight into aqueous process in chemistry and biology.² Many of these studies have been motivated by compelling need to understand liquid water, and how molecular clusters evolve into liquid state.

The pentamer of water, $(\text{H}_2\text{O})_5$ has received considerable attention^{2,6-9} due to its interesting dynamics, chirality and the fact that the pentagonal rings of water molecules occur in nature as calthrate hydrates and solvation of hydrophobic groups in biosystems. Furthermore, a five-membered cluster of water seems to have a dominant population and role in liquid water simulations. For these reasons $(\text{H}_2\text{O})_5$ has been the focus of several spectroscopic studies.⁶⁻⁹ Liu et al.⁸ have employed terahertz laser spectroscopy for detailed analysis of vibration-rotation-tunneling spectra of $(\text{D}_2\text{O})_5$. The spectra revealed that although the pentamer exhibits a chiral asymmetric five-member ring geometry as its equilibrium structure (shown in Fig.1), the observed spectra of $(\text{D}_2\text{O})_5$ are consistent with a pseudorotation model that yields averaged rotational constants that correspond to an achiral quasi-planar C_{5h} oblate top geometry. The authors⁸ have also noted that facile flipping motions of protons are feasible due to low barriers and that should yield a non-rigid pentamer, especially for the protonated form. In a more recent study Keutsch and Saykally² have shown that for the pentamer, which has a chiral equilibrium structure, allows for very facile torsional tunneling motions and thus bifurcation tunneling splitting which connects 32 degenerate minima have been observed in $(\text{H}_2\text{O})_5$ although somewhat reduced compared to $(\text{H}_2\text{O})_3$. The most recent study on water clusters by Goldman and Saykally¹ deals with diffusion Monte Carlo methods for ground vibrational properties of water clusters.

As noted by the above survey, water clusters in general, and the water pentamer in particular exhibit non-rigid tunneling motions among several potential minima separated by surmountable energy barriers. Although the extent of tunneling would depend on the actual barriers, there is a compelling need to consider the molecular symmetry groups of the non-rigid cluster from semi-rigid to fully non-rigid limits. Longuet-Higgins¹⁶ has formulated the symmetry groups of non-rigid molecules as permutation-inversion groups by including all feasible permutations of the nuclei under such fluxional or tunneling motions. Up to now the full character table of the fully non-rigid (H₂O)₅ pentamer has not been obtained. The present author has shown that the groups of non-rigid molecules can be expressed as wreath product groups and as generalized wreath products.^{15,17-20} These groups have also been used in a number of chemical applications such as enumeration of isomers,^{23,24} weakly-bound van der Waals or hydrogen-bonded complexes such as (NH₃)₂, (H₂O)₂, (C₆H₆)₂, etc.,^{12-15,21} polyhedral structures,^{25,26} spectroscopy,^{21,22,13,14} and clusters.²⁷ King^{25,26} has applied the wreath product groups to represent the symmetries of four-dimensional analogues of polyhedra. Thus apart from the current motivation of (H₂O)₅ there is considerable interest in the wreath product groups of higher order and their character tables. The present author¹⁵ has applied combinatorial methods without the construction of the character tables for the spin statistics of protonated forms of water clusters. However, the character tables, tunneling splittings and correlation of the rotational and rovibronic levels from semi-rigid to non-rigid limits have not been considered as character tables of the larger groups such as the one for (H₂O)₅ have not been derived.

In this study, we have considered the development of the character table of the non-rigid (H₂O)₅ in its full non-rigid limit. By this it is meant that all possible “flippings” or permutations of the protons on each water molecule are considered. Since the barriers for such motions are surmountable depending on the experimental conditions, the full group would comprise of all feasible permutations of protons arising from the flipping motion on each water and the permutations of the water molecules. The resulting group is shown to be the wreath product $S_5[S_2]$, where the group S_n is a permutation group of $n!$ operations, and the square bracket symbol stands for wreath products. We show that the fully non-rigid (H₂O)₅ exhibits a group of 3840 operations divided into 36 conjugacy

classes and 36 irreducible representations. We have obtained the character table of this group for the first time, and we have applied the character table to correlate the rotational levels and nuclear spin statistical weights from a semi-rigid $(\text{H}_2\text{O})_5$ to a fully non-rigid $(\text{H}_2\text{O})_5$. The nuclear spin statistical weights show that only some of the tunneling levels are significantly populated.

2 Wreath Product Group $S_5[S_2]$ for $(\text{H}_2\text{O})_5$.

Although the theory of wreath product groups and the related mathematical details have been described in sufficient details elsewhere,^{17,18} we provide here salient points so that the work is sufficiently self-contained relative to $(\text{H}_2\text{O})_5$. All our illustrations will be restricted only to $(\text{H}_2\text{O})_5$. Suppose G is a group of permutations of some nuclei and H be another permutation group of nuclei. For the case of $(\text{H}_2\text{O})_5$ the group G consists of the permutations of the oxygen nuclei in the fully non-rigid limit where they are allowed to exchange and H is the permutations of the protons due to the facile flipping motion. Thus the group G is the set of $5!$ permutations of five O nuclei, and H is the group S_2 of protons on each water molecule that correspond to the flipping motion which exchanges these protons. In general the permutation S_n group²⁸⁻³⁰ consists of $n!$ permutations of n objects in a set Ω of chosen nuclei in the molecule to represent the rigid framework. Note that the notation S_n that we use here differs from the point group S_n that corresponds to an n -fold improper axis of rotation. All references to S_n in this work would mean the permutation group of $n!$ operations. As the oxygen atoms get permuted it also carries with it the protons attached to it, and thus induces permutations of the protons also. Consequently, the overall group of $(\text{H}_2\text{O})_5$ becomes the wreath product of G with H , denoted by $G[H]$, which becomes $S_5[S_2]$ in this case. The wreath product group $G[H]$ is defined as the set of permutations

$$\{(g;\pi) | \pi \text{ mapping of } \Omega \text{ into } H, g \in G\}$$

such that the product of two permutations is defined as

$$(g;\pi)(g';\pi') = (gg';\pi\pi'_g),$$

where

$$\pi_g(i) = \pi(g^{-1}i), \forall i \in \Omega,$$

$$\pi\pi'(i) = \pi(i)\pi'(i), \forall i \in \Omega.$$

An element of $G[H]$ is represented by $(g; h_1, h_2, \dots, h_n)$, where $g \in G$ and $h_i \in H$. Thus the group $G[H]$ contains $|G||H|^n$ elements where n is the order of Ω . In the case of $(H_2O)_5$ the full non-rigid permutation group's order is given by

$$|S_5[S_2]| = 5! (2!)^5 = 3840.$$

The Group $S_5[S_2]$ is isomorphic with

$$S_5[S_2] = (S_2 \times S_2 \times S_2 \times S_2 \times S_2) \wedge S_5',$$

where five copies of the same group S_2 are multiplied, \times symbol stands for direct product while \wedge symbol represents a semi-direct product..

The conjugacy classes of wreath product $S_5[S_2]$ group are obtained as matrix types from the permutation cycle type or orbit structure of g in S_5 and the conjugacy class information of S_2 . Let a permutation $g \in S_5$ generate a_1 cycles of length 1, a_2 cycles of length 2, ..., a_5 cycles of length 5 upon its action on the set Ω . The cycle type of g is then denoted by $T_g = (a_1, a_2, \dots, a_5)$. To illustrate a permutation $(12)(345)$ of the oxygen nuclei would have the cycle type $(0, 1, 1, 0, 0)$ as it generates one cycle of length 2 and one cycle of length 3. Since there are only 2 conjugacy classes for S_2 we may denote them by C_1 and C_2 . The cycle type of an element in the wreath product $S_5[S_2]$ can be expressed by a 2×5 matrix, $T(g; \pi)$ also known as the cycle type of $(g; \pi)$. It is obtained by investigating the orbit structure of g and the conjugacy class of S_2 . That is, suppose a_{ik} of the cycle products of g belong to the conjugacy class C_i , we obtain the cycle type of $(g; \pi)$, which represents the conjugacy class of $S_5[S_2]$ as

$$T(g; \pi) = a_{ik} \quad (1 \leq i \leq 2, 1 \leq k \leq 5).$$

Table I shows all of the cycle matrix types for the conjugacy classes of the non-group of $(H_2O)_5$, viz., the $S_5[S_2]$ group. Let $P(m)$ denote the number of partitions of integer m with the convention that $P(0) = 1$. Let 5 be partitioned into ordered pairs as there are only 2 conjugacy classes in the S_2 group, denoted by $(n) = (n_1, n_2)$ such that

$\sum_i n_i = n$. Hence the number of conjugacy classes of $S_5[S_2]$ are given by

$$\sum_n P(n_1)P(n_2)$$

The ordered partitions of 5 into 2 parts are (5,0), (0,5), (4,1), (1,4), (3,2), and (2,3) since the S_2 group has 2 conjugacy classes. Substituting the values of $P(5)=7$, $P(4)=5$, $P(3)=2$, $P(2)=2$ and $P(0)=1$ in the above expression we obtain the number of conjugacy classes of $S_5[S_2]$ as $2 \times 7 + 2 \times 4 + 2 \times 3 \times 2 = 36$. All 36 conjugacy classes of the $S_5[S_2]$ group are shown in Table I. The number of elements in each conjugacy class of $S_n[S_2]$ is given by

$$\frac{n!2^n}{\prod_{i,k} a_{ik}!(2k)^{a_{ik}}}$$

To illustrate consider the number of elements in the tenth conjugacy class with the matrix

type $\begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \end{bmatrix}$ is given by

$$\frac{5!(2!)^5}{2!(2.1)^2 1!(2.1)^1 1!(2.2)^1} = 60$$

Thus $5!2^5=3840$ operations are divided into 36 conjugacy classes with number of elements in each class obtained using the above formula. All conjugacy classes together with their cycle types and the number of elements in each class are shown in Table I.

Next we obtain the character table of the $S_5[S_2]$ group with combinatorial matrix generating function that use matrix type polynomials. All possible irreducible representations of the $S_5[S_2]$ group can be derived using induced representations from a smaller group to a larger group. The irreducible representations of the S_n group^{28,30} are represented by the partitions of n , denoted by $[n_1 \ n_2 \dots n_m]$, where n_1, n_2, \dots, n_m is a partition of the integer n . Thus the irreducible representations of the S_5 group are given by $[5]$, $[41]$, $[32]$, $[31^2]$, $[2^2 \ 1]$, $[21^3]$, and $[1^5]$ while the S_2 group has only $[2]$ and $[1^2]$ representations. The irreducible representations of $S_5[S_2]$ are constructed by first forming

the outer tensor (outer direct) products of the irreducible representations of S_2 5 times, then finding the inertia factor of each such product, and subsequently inducing the representation from the inertia factor group to the whole group. First the unique outer products for the irreducible representations of $S_2 \times S_2 \times S_2 \times S_2 \times S_2$ are constructed as

$[2] \# [2] \# [2] \# [2] \# [2]$, $[2] \# [2] \# [2] \# [2] \# [1^2]$, $[2] \# [2] \# [2] \# [1^2] \# [1^2]$, $[2] \# [2] \# [1^2] \# [1^2]$, $[1^2]$ and $[2] \# [1^2] \# [1^2] \# [1^2] \# [1^2]$ and $[1^2] \# [1^2] \# [1^2] \# [1^2] \# [1^2]$.

The inertia factor groups (subgroup of S_5) of the above six products are S_5' , $S_4 \times S_1'$ (identity group), $S_3 \times S_2'$, $S_2 \times S_3'$, $S_1 \times S_4'$ and S_5' respectively. All representations of the $S_5[S_2]$ groups are obtained by multiplying the unique outer products of irreducible representations as obtained above with the irreducible representations of the factor group G' for each product, and then inducing the whole representation into $S_5[S_2]$. In symbols the irreducible representations are given by

$$F^* = (F_1 \# F_2 \# \dots \# F_5) \otimes F' \uparrow S_5[S_2],$$

where $F_1 \# F_2 \# \dots \# F_5$ is the outer tensor product of the irreducible representations (F_1, F_2, \dots, F_5) from the Group S_2 , $\#$ is the outer product, F' is an irreducible representation of the factor group G' , \otimes represents an inner product, and the \uparrow stands for an induced representation to the whole group $G[H]$. Table II shows all 36 irreducible representations thus enumerated for the $S_5[S_2]$ group together with labels for the irreducible representations according to the dimensions of the representations.

The character table of the $S_5[S_2]$ group is generated using the generating functions as polynomials of matrix cycle types. The present author¹⁸ has developed a general algorithm for the characters of the wreath product groups. Let P_G^χ be the generalized character cycle index polynomial of the irreducible representation χ of the factor subgroup G' of G , given by

$$P_G^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g) s_1^{b_1} s_2^{b_2} \dots s_n^{b_n}$$

Let $T(M)_i$ be the matrix type of the representation of the inertia factor. The generating function for the irreducible representation F^* of $S_n[S_2]$ is obtained by the replacement:

$$T(G[H])^{F^*} = P_G^{\chi}(s_i \rightarrow T(M)_i)$$

In the above expression every s_i is replaced by the corresponding matrix type $T(M)_i$, where all algebraic manipulations are done with the cycle type matrices. We have introduced $\oplus, \otimes, -$ operations for additions, multiplications and subtractions to contrast that these are not ordinary matrix multiplications, etc.

We shall illustrate this procedure with a few examples. Consider the G_1 irreducible representation given by $([2]^5) \otimes [41]'$. The generalized character cycle index of $[41]'$, the factor group irreducible representation, is given by

$$P_{S_5}^{[41]} = \frac{1}{120} [4s_1^5 + 20s_1^3s_2 + 20s_1^2s_3 - 20s_2s_3 - 24s_5]$$

For the representation $[2]$, the matrix type expressions $T(M)_i$ are given as follows:

$$\begin{aligned} T(M)_1^{[2]} &= \frac{1}{2} \left[\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} \right] \\ T(M)_2^{[2]} &= \frac{1}{2} \left[\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} \right] \\ T(M)_3^{[2]} &= \frac{1}{2} \left[\begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \right] \\ T(M)_4^{[2]} &= \frac{1}{2} \left[\begin{bmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \right] \\ T(M)_5^{[2]} &= \frac{1}{2} \left[\begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \right] \end{aligned}$$

Replacing every s_i by $T(M)_i$ in the expression for $P_{S_5}^{[41]}$ we obtain

$$\begin{aligned}
GF_{G_1} = & \frac{1}{5!} \left[4 \left\{ \frac{1}{2} \left[\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} \right] \right\}^5 \right. \\
& + 20 \left\{ \frac{1}{2} \left[\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} \right] \right\}^3 \\
& \frac{1}{2} \left[\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} \right] - 20 \frac{1}{2} \left[\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} \right] \\
& \times \frac{1}{2} \left[\begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \right] - 24 \frac{1}{2} \left[\begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \right] \Big]
\end{aligned}$$

Using the matrix manipulations for the cycle types where the multiplication of two matrix cycle types is interpreted as ordinary matrix additions, we can simplify the above expression as

$$\begin{aligned}
GF_{G_1} = & \frac{1}{5!} \frac{1}{2^5} \left\{ 4 \begin{bmatrix} 5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} + 20 \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} + 40 \begin{bmatrix} 3 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix} + 40 \begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \end{bmatrix} \right. \\
& + 20 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & 0 \end{bmatrix} + 4 \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & 0 \end{bmatrix} + 40 \begin{bmatrix} 3 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} + 40 \begin{bmatrix} 3 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} \\
& + 120 \begin{bmatrix} 2 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} + 120 \begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \end{bmatrix} + 120 \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix} + 120 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 2 & 1 & 0 & 0 & 0 \end{bmatrix} + \\
& 40 \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \end{bmatrix} + 40 \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 3 & 1 & 0 & 0 & 0 \end{bmatrix} + 80 \begin{bmatrix} 2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} + 80 \begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \\
& + 160 \begin{bmatrix} 1 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} + 160 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \end{bmatrix} + 80 \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix} + 80 \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 1 & 0 & 0 \end{bmatrix} \\
& - 160 \begin{bmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} - 160 \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} - 160 \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} - 160 \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \end{bmatrix} \\
& \left. - 384 \begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} - 384 \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \right\}
\end{aligned}$$

The expression thus obtained above for the G_1 representation generates the character values in that the coefficients of the various matrix types when sorted out according to the order of the conjugacy classes in Table I gives the character values multiplied by the

order of the corresponding conjugacy class with the order of the group (3840) factored out. Consequently, the following string of coefficients is obtained after dividing the coefficients in the above expression by the order of each conjugacy class:

{4 4 4 4 4 4 2 2 2 2 2 2 2 2 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 -1 -1 -1 -1 -1 -1}

This string yields the character values for the G_1 representation. In this manner, we obtain the character string for all 36 representations shown in Table II. This of course involves considerable algebraic manipulations for all 36 irreducible representations, and all of these character values were computed manually. The character table thus constructed is shown in Table III.

As can be seen from Table III, the character table of $S_5[S_2]$ or G_{3840} contains 36 irreducible representations. There are 4 one-dimensional, 4 four-dimensional, 8 five-dimensional, 2 six-dimensional, 10 ten-dimensional, 4 15-dimensional and 4 20-dimensional irreducible representations in the group which satisfy

$$4 \times 1^2 + 4 \times 4^2 + 8 \times 5^2 + 2 \times 6^2 + 10 \times 10^2 + 4 \times 15^2 + 4 \times 20^2 = 3840$$

The above condition is a requirement of the great orthogonality theorem. Moreover, we ensured that all the character values of 36 irreducible representations are orthogonal to each other by a computer code. This exhaustive checks involved 630 pairs of checks, and all of these checks produced correct zero overlaps for the irreducible representations shown in Table III confirming that the numbers are correct. Another important check is that the sum of squares of numbers multiplied by the corresponding orders of conjugacy classes in any row should add up to 3840. This result was also used to verify the correctness of all numbers in Table III. All of these confirm that the numbers in Table III are correct.

3. Nuclear spin statistics, Tunneling Splittings of rotational/rovibronic levels and of $(H_2O)_5$ from semi-rigid to fully non-rigid limits.

We consider the use of the character table for water pentamer in fully non-rigid limit. Liu et al.⁸ have obtained vibrational-rotation-tunneling spectra of the deuterated water pentamer, $(D_2O)_5$. In its deuterated form the cluster behaves as a quasi-planar oblate top with an averaged C_{5h} symmetry. We call this a semi-rigid structure in that the equilibrium geometry of the completely rigid structure, which is shown in Fig1, is of C_1 symmetry and its chiral. The tunneling motions in the deuterated form in the ground state

are restricted to certain pseudorotations, which yield an overall averaged symmetry of C_{5h} or a G_{10} molecular symmetry group as noted by Liu et al.⁸ For the fully protonated form quantum tunneling among all 32 possible minima that arise from the flipping of the hydrogen atoms which yield $2^5=32$ permutations have been observed. Thus we provide complete analysis of the rotational levels, tunneling splittings and nuclear spin statistical weights of the rovibronic levels in both the semi-rigid and fully non-rigid wreath product group limits of $(H_2O)_5$.

Table IV shows the correlation of the rotational levels of the pentamer in both the semi-rigid and non-rigid groups. Note that fully rigid structure (Fig. 1) has only C_1 symmetry and thus all the irreducible representations of the non-rigid group will correlate into the rigid structure. Moreover, it is highly unlikely that the cluster will retain its rigid C_1 geometry in view of quantum tunneling. Liu et al.⁸ have contrasted the parts of the degenerate representation E_1 and E_2 in the C_{5h} symmetry, since the accidental degeneracies may be split by Coriolis coupling. However for the analysis of nuclear spin statistical weights or the tunneling splittings it is not necessary to make the distinction between the degenerate parts of the E_1 and E_2 representations of the semi-rigid group, and it is suggested that the tunneling levels obtained using the correlation may be further contrasted according to other perturbations such as Coriolis coupling. Hence we do all our analysis of tunneling splittings in C_5 and $S_5[S_2]$ groups. In fact C_5 group is sufficient for the correlation of levels, as the horizontal plane does not generate any new permutation of the proton nuclei. As seen from Table IV, we obtain a pattern for the rotational levels into tunneling levels both in the semi-rigid and non-rigid limits. There is a period of 5 that arises from the symmetry of the semi-rigid molecule. A large number of tunneling levels arise for each of the rotational level in the fully non-rigid limit. However as we show below only a few of those levels are populated by nuclear spins for the protonic form of the pentamer although for the deuterated form more tunneling levels are populated.

Next we consider the nuclear spin statistics of the pentamer both in its protonated and deuterated forms. Following this we shall consider the correlation of rovibronic levels into tunneling levels together with the nuclear spin statistical weights. From the character table we can construct the combinatorial generating functions to enumerate the

nuclear spin functions that transform according to the given irreducible representation. This information can be sorted out into nuclear spin multiplets from which we can derive the frequencies of various irreducible representations in all nuclear spin functions. Then we shall use the Pauli exclusion principle for the protons, which are fermions and thus the overall function must be antisymmetric. For the bosons such as deuterium nuclei, the overall function must be symmetric. Let us illustrate the technique with $(D_2O)_5$. Let us represent three m_s functions of the D nucleus by λ , μ , and ν , where these labels represent $m_s = -1, 0$ and $+1$, respectively. Let us consider the G_1 representation in character table III for which we obtain the GGCI of the representation as

$$GF_{G_1} = \frac{1}{5!} \frac{1}{2^5} \{ 4s_1^{10} + 20s_1^8 s_2 + 40s_1^6 s_2^2 + 40s_1^4 s_2^3 + 20s_1^2 s_2^4 + 4s_2^5 + 40s_1^6 s_2^2 + 40s_1^6 s_4 + 120s_1^2 s_2^3 + 120s_1^4 s_2 s_4 + 120s_1^2 s_2^4 + 120s_1^2 s_2^2 s_4 + 40s_2^5 + 40s_2^3 s_4 + 80s_1^4 s_2^3 + 80s_1^4 s_6 + 160s_1^2 s_2^3 s_2 + 160s_1^2 s_2 s_6 + 80s_2^2 s_3^2 + 80s_2^2 s_6 - 160s_2^2 s_3^2 - 160s_2^2 s_6 - 160s_4 s_3^2 - 160s_4 s_6 - 384s_5^2 - 384s_{10} \}$$

The 3D nuclear spin generating function is obtained by replacing every s_k in the above expression by $(\lambda^k + \mu^k + \nu^k)$. Thus we obtain

$$P^{G_1} = \frac{1}{3840} \left[4(\lambda + \mu + \nu)^{10} + 20(\lambda + \mu + \nu)^8 (\lambda^2 + \mu^2 + \nu^2) + 40(\lambda + \mu + \nu)^6 (\lambda^2 + \mu^2 + \nu^2)^2 + 40(\lambda + \mu + \nu)^4 (\lambda^2 + \mu^2 + \nu^2)^3 + 20(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2)^4 + 4(\lambda^2 + \mu^2 + \nu^2)^5 + 40(\lambda + \mu + \nu)^6 (\lambda^2 + \mu^2 + \nu^2)^2 + 40(\lambda + \mu + \nu)^6 (\lambda^4 + \mu^4 + \nu^4)^1 + 120(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2)^3 + 120(\lambda + \mu + \nu)^4 (\lambda^2 + \mu^2 + \nu^2) (\lambda^4 + \mu^4 + \nu^4) + 120(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2)^4 + 120(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2)^2 (\lambda^4 + \mu^4 + \nu^4) + 40(\lambda^2 + \mu^2 + \nu^2)^5 + 40(\lambda^2 + \mu^2 + \nu^2)^3 (\lambda^4 + \mu^4 + \nu^4) + 80(\lambda + \mu + \nu)^4 (\lambda^3 + \mu^3 + \nu^3)^2 + 80(\lambda + \mu + \nu)^4 (\lambda^6 + \mu^6 + \nu^6) + 160(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2) (\lambda^3 + \mu^3 + \nu^3)^2 + 160(\lambda + \mu + \nu)^2 (\lambda^2 + \mu^2 + \nu^2) (\lambda^6 + \mu^6 + \nu^6) + 80(\lambda^2 + \mu^2 + \nu^2)^2 (\lambda^3 + \mu^3 + \nu^3)^2 + 80(\lambda^2 + \mu^2 + \nu^2)^2 (\lambda^6 + \mu^6 + \nu^6) - 160(\lambda^2 + \mu^2 + \nu^2)^2 (\lambda^3 + \mu^3 + \nu^3)^2 - 160(\lambda^4 + \mu^4 + \nu^4) (\lambda^3 + \mu^3 + \nu^3)^2 - 160(\lambda^4 + \mu^4 + \nu^4) (\lambda^6 + \mu^6 + \nu^6) - 384(\lambda^5 + \mu^5 + \nu^5)^2 - 384(\lambda^{10} + \mu^{10} + \nu^{10}) \right]$$

Once the above expression is simplified, the coefficient of a typical term $\lambda^i \mu^j \nu^k$ yields the number of ^3D nuclear spin functions containing i spin functions with $m_s=-1$, j functions with $m_s=0$ and k spin functions with $m_s=+1$ that transform according to the G_2 irreducible representation. We sort the spin functions according to their total M_F nuclear spin quantum numbers which yield the various nuclear spin multiplets for $(\text{D}_2\text{O})_5$ corresponding to the G_1 irreducible representation. We can obtain the corresponding results for the protonated form of water pentamer by replacing every s_k by $(\alpha^k + \beta^k)$ in the cycle index polynomial (above) for the G_2 representation. The results thus obtained are shown in Table IV for both $(\text{H}_2\text{O})_5$ and $(\text{D}_2\text{O})_5$.

We can also obtain the total nuclear spin statistical weights from the nuclear spin species enumerated in Table V. As seen from Table V and as expected, the proton nuclear spin multiplets occur with fewer frequencies as compared to the deuterium spin species. The nuclear spin statistical weights are obtained by first finding the frequencies of each of the irreducible representations. This is accomplished by multiplying the spin multiplicity by the frequency of each multiplet, and adding the all of the numbers. Consequently, we obtain the frequencies of the various irreducible representations for the H and D nuclear spin functions as follows:

$$\begin{aligned}\Gamma_{\text{H}} = & 21\text{A}_1 + 0\text{A}_2 + \text{A}_3 + 0\text{A}_4 + 24\text{G}_1 + 0\text{G}_2 + 0\text{G}_3 + 0\text{G}_4 + \\ & 15\text{H}_1 + 3\text{H}_2 + 0\text{H}_3 + 0\text{H}_4 + 15\text{H}_5 + 0\text{H}_6 + 3\text{H}_7 + 0\text{H}_8 + 6\text{I}_1 \\ & + 0\text{I}_2 + 6\text{M}_1 + 0\text{M}_2 + 10\text{M}_3 + 1\text{M}_4 + 0\text{M}_5 + 0\text{M}_6 + 6\text{M}_7 + 0\text{M}_8 + 3\text{M}_9 + 0\text{M}_{10} \\ & + 15\text{R}_1 + 3\text{R}_2 + 0\text{R}_3 + 0\text{R}_4 + 8\text{W}_1 + 0\text{W}_2 + 0\text{W}_3 + 0\text{W}_4\end{aligned}$$

$$\begin{aligned}\Gamma_{\text{D}} = & 252\text{A}_1 + 6\text{A}_2 + 21\text{A}_3 + 0\text{A}_4 + 504\text{G}_1 + 84\text{G}_2 + 24\text{G}_3 + 0\text{G}_4 + \\ & 420\text{H}_1 + 210\text{H}_2 + 15\text{H}_3 + 3\text{H}_4 + 378\text{H}_5 + 45\text{H}_6 + 90\text{H}_7 + 0\text{H}_8 + \\ & 336\text{I}_1 + 6\text{I}_2 + 315\text{M}_1 + 36\text{M}_2 + 336\text{M}_3 + 120\text{M}_4 + 168\text{M}_5 + 60\text{M}_6 + 210\text{M}_7 + 21\text{M}_8 + \\ & 150\text{M}_9 + 15\text{M}_{10} + 630\text{R}_1 + 315\text{R}_2 + 90\text{R}_3 + 18\text{R}_4 + 420\text{W}_1 + 210\text{W}_2 + \\ & 168\text{W}_3 + 120\text{W}_4\end{aligned}$$

The overall nuclear spin statistical weights are obtained using the above frequencies and stipulating that the overall wavefunction must be antisymmetric for fermions in compliance with the Pauli exclusion principle for $(\text{H}_2\text{O})_5$. This means the overall wave function must transform as the A_3 irreducible representation for $(\text{H}_2\text{O})_5$ in table III which has the character values of -1 for all odd exchanges of nuclei. The nuclear spin statistical weights of the tunneling levels are thus obtained by using result as $A_1(1)$, $A_2(0)$, $A_3(21)$, $A_4(0)$, $G_1(0)$, $G_2(0)$, $G_3(24)$, $G_4(0)$, $H_1(0)$, $H_2(0)$, $H_3(15)$, $H_4(3)$, $H_5(3)$, $H_6(0)$, $H_7(15)$, $H_8(0)$, $I_1(0)$, $I_2(6)$, $M_1(0)$, $M_2(6)$, $M_3(6)$, $M_4(0)$, $M_5(3)$, $M_6(0)$, $M_7(10)$, $M_8(1)$, $M_9(0)$, $M_{10}(0)$, $R_1(0)$, $R_2(0)$, $R_3(15)$, $R_4(3)$, $W_1(0)$, $W_2(0)$, $W_3(8)$, and $W_4(0)$. The nuclear spin statistical weights of the deuterated forms are obtained likewise with the exception that the overall wavefunction must be symmetric as $(\text{D}_2\text{O})_5$ consists of bosons and thus the total wavefunction must transform as A_1 . By using this together with the frequencies of the irreducible representations, we have obtained the nuclear spin statistical weights of the deuterated and protonated forms which are shown in Table VI.

As noted by Liu et al.⁸ the VRT spectra exhibit averaged rotational constants that seem to fit into a semi-rigid pseudorotation model of $(\text{D}_2\text{O})_5$. This corresponds to an averaged quasi-planar structure for $(\text{D}_2\text{O})_5$ or a C_{5h} symmetry. Since D nuclei are heavier all possible tunneling motions may not be feasible and thus we have also obtained the nuclear spin statistical weights and group theoretical tunneling analysis of both protonated and deuterated forms in the C_{5h} symmetry. Since the horizontal plane does not generate any new nuclear permutations of protons (deuterium nuclei), it suffices to analyze the nuclear spin statistical weights and tunneling splittings in the C_5 subgroup. If the weights are needed for each of the degenerate components of the E_1 and E_2 representations individually, the total weights are divided by 2. Thus we have provided our analysis primarily in C_5 and further in fully non-rigid $S_5[S_2]$ groups.

Table VII shows the correlation of the rovibronic levels from the semi-rigid C_{5h} symmetry to fully non-rigid $S_5[S_2]$ correlation of $(\text{H}_2\text{O})_5$. Note that the correlation from the fully-rigid chiral equilibrium structure with C_1 symmetry would involve every irreducible representation of the $S_5[S_2]$ non-rigid group and hence it is straight forward. The correlation table shown in Table VII reveals that the A_1 rovibronic level is split into many tunneling levels. However, only some of the tunneling levels have non-zero

nuclear spin statistical weights and would thus be populated. They are A_1 , A_3 , H_3 , H_4 , H_5 , H_7 , I_2 , M_2 , M_3 , M_5 , M_7 , M_8 , R_3 , R_4 , and W_3 tunneling levels, as seen from Table VII. Thus primarily 15 tunneling levels have non-zero nuclear spin populations for $(H_2O)_5$ in its fully non-rigid ground state. The excited rovibronic states of $(H_2O)_5$ would of course have E_1 and E_2 symmetries that correlate according to the tunneling species in Table VII. Note that E_1 and E_2 representations have the same spin statistics and tunneling patterns due to the accidental degeneracy of the 2 irreducible representations which yield the same cycle index polynomials. In order to observe nuclear spin multiplets one needs much higher resolution spectra that have the capabilities to resolve hyperfine structural patterns. Such spectra are available on smaller clusters and it is hoped that in future hyperfine structures in higher clusters may become observable.

4. Conclusion

In this study we have formulated the permutation group of $(H_2O)_5$ as the wreath product $S_5[S_2]$ with 3840 elements and its complete character table has been obtained for the first time. It was shown that the group has 36 conjugacy classes characterized by powerful matrix cycle types and 36 irreducible representations. The character values of the irreducible representations were obtained using powerful matrix-cycle type combinatorial generating functions. The character table thus constructed was used to generate the nuclear spin multiplets of both $(H_2O)_5$ and $(D_2O)_5$ using powerful generating functions. The tunneling splittings of the rotational levels were also obtained in the semi-rigid C_{5h} group and fully non-rigid $S_5[S_2]$ groups. We have shown that only 15 tunneling levels have non-zero nuclear spin statistical weights in the ground rovibronic state of $(H_2O)_5$. We have also obtained the correlation tables for all rotational and rovibronic levels of $(H_2O)_5$ by using the induced representation techniques. It was shown that more tunneling levels are obtained in the fully non-rigid limit of $(H_2O)_5$ compared to the quasi-planar C_{5h} model for the semi-rigid $(D_2O)_5$ which appears to exhibit restricted pseudorotation. It is hoped that the present study would stimulate further search for spectra with higher resolution that contain hyperfine features especially for $(H_2O)_5$. Such

spectral data may reveal the extent of non-rigidity and nuclear hyperfine patterns for $(\text{H}_2\text{O})_5$.

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Figure Caption

Fig 1 Equilibrium Geometry of $(\text{H}_2\text{O})_5$ in its cyclic chiral form with no symmetry.

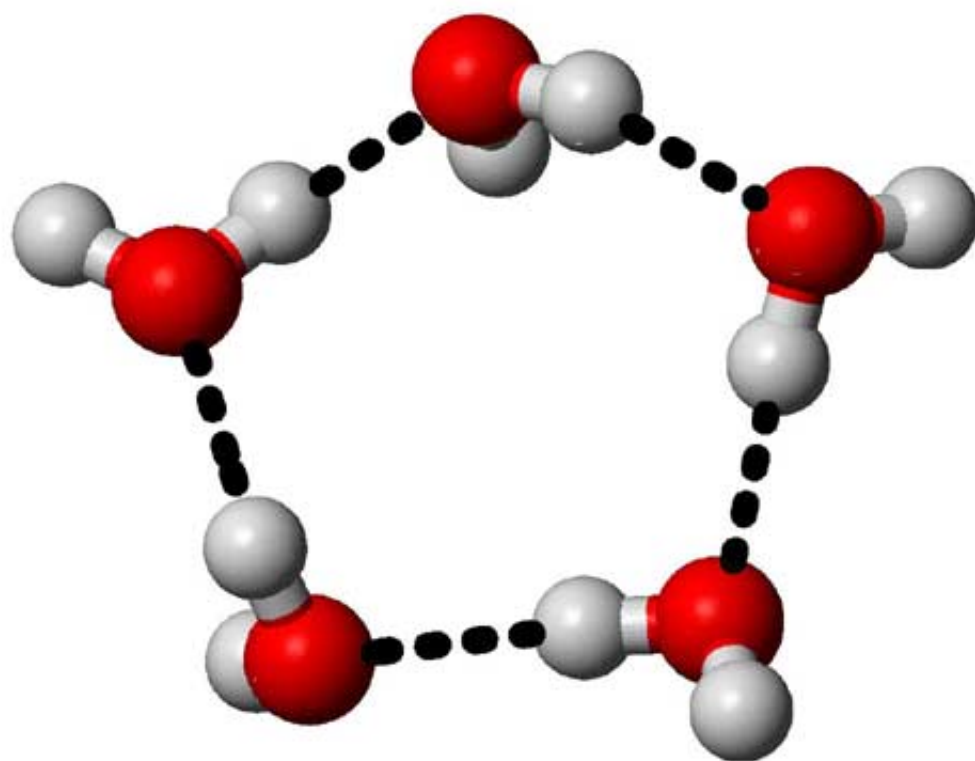


Table I Conjugacy Classes of the $S_5[S_2]$ group

No	Matrix type	Permutation	Number of elements	No	Matrix type	Permutation	Number of elements
1	$\begin{bmatrix} 5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	1^{10}	1	2	$\begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^8 2$	5
3	$\begin{bmatrix} 3 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^6 2^2$	10	4	$\begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^4 2^3$	10
5	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2^4$	5	5	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & 0 \end{bmatrix}$	2^5	1
7	$\begin{bmatrix} 3 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^6 2^2$	20	8	$\begin{bmatrix} 3 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix}$	$1^6 4$	20
9	$\begin{bmatrix} 2 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^4 2^3$	60	10	$\begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \end{bmatrix}$	$1^4 2 4$	60
11	$\begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2^4$	60	12	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 2 & 1 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2^2 4$	60
13	$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 \end{bmatrix}$	2^5	20	14	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 3 & 1 & 0 & 0 & 0 \end{bmatrix}$	$2^3 4$	20
15	$\begin{bmatrix} 2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^4 3^2$	80	16	$\begin{bmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}$	$1^4 6$	80
17	$\begin{bmatrix} 1 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2 3^2$	160	18	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \end{bmatrix}$	$1^2 2 6$	160

No	Matrix type	Permutation	Number of elements	No	Matrix type	Permutation	Number of elements
19	$\begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \end{bmatrix}$	$3^2 2^2$	80	20	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 1 & 0 & 0 \end{bmatrix}$	$2^2 6$	80
21	$\begin{bmatrix} 1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2^4$	60	22	$\begin{bmatrix} 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$	2^5	60
23	$\begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix}$	$1^2 2^2 4$	120	24	$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \end{bmatrix}$	$2^3 4$	120
25	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \end{bmatrix}$	$1^2 4^2$	60	26	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 \end{bmatrix}$	24^2	60
27	$\begin{bmatrix} 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$1^2 4^2$	240	28	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix}$	$1^2 8$	240
29	$\begin{bmatrix} 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix}$	24^2	240	30	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \end{bmatrix}$	2^8	240
31	$\begin{bmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$2^2 3^2$	160	32	$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}$	$2^2 6$	160
33	$\begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix}$	$4^2 3$	160	34	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \end{bmatrix}$	$4^2 6$	160
35	$\begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	5^2	384	36	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$	10	384

Table II Irreducible Representations of the $S_5[S_2]$ group.

Label	Irreducible Representation	Dimension
A ₁	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[5]'$	1
G ₁	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[41]'$	4
H ₁	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[32\ 1]'$	5
I ₁	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[31^2]'$	6
H ₂	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[2^21\ 1]'$	5
G ₂	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[21^3]'$	4
A ₂	$([2]\#[2]\#[2]\#[2]\#[2])\otimes[1^5]'$	1
G ₁	$([2]\#[2]\#[2])\otimes[3\ 1]'$ $\#[1^2]\otimes[1]'$	4
A ₃	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[5]'$	1
G ₃	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[41]'$	4
H ₃	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[32\ 1]'$	5
I ₂	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[31^2]'$	6
H ₄	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[2^21\ 1]'$	5
G ₄	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[21^3]'$	4
A ₄	$([1^2]\#[1^2]\#[1^2]\#[1^2]\#[1^2])\otimes[1^5]'$	1
H ₅	$([2]^4)\otimes[4]'\#[1^2]\otimes[1]'$	5
R ₁	$([2]^4)\otimes[31]'\#[1^2]\otimes[1]'$	15
M ₁	$([2]^4)\otimes[2^2]'\#[1^2]\otimes[1]'$	10
R ₂	$([2]^4)\otimes[21^2]'\#[1^2]\otimes[1]'$	15
H ₆	$([2]^4)\otimes[1^4]'\#[1^2]\otimes[1]'$	5
H ₇	$([1^2]^4)\otimes[4]'\#[2]\otimes[1]'$	5
R ₃	$([1^2]^4)\otimes[31]'\#[2]\otimes[1]'$	15
M ₂	$([1^2]^4)\otimes[2^2]'\#[2]\otimes[1]'$	10
R ₄	$([1^2]^4)\otimes[21^2]'\#[2]\otimes[1]'$	15
H ₈	$([1^2]^4)\otimes[1^4]'\#[2]\otimes[1]'$	5
M ₃	$([2]^3)\otimes[3]'\#[1^2]^2\otimes[2]'$	10
W ₁	$([2]^3)\otimes[21]'\#[1^2]^2\otimes[2]'$	20
M ₄	$([2]^3)\otimes[1^3]'\#[1^2]^2\otimes[2]'$	10
M ₅	$([2]^3)\otimes[3]'\#[1^2]^2\otimes[1^2]'$	10
W ₂	$([2]^3)\otimes[21]'\#[1^2]^2\otimes[1^2]'$	20
M ₆	$([2]^3)\otimes[1^3]'\#[1^2]^2\otimes[1^2]'$	10

M_7	$([1^2]^3) \otimes [3]' \# ([2]^2 \otimes [2]')$	10
W_3	$([1^2]^3) \otimes [21]' \# ([2]^2 \otimes [2]')$	20
M_8	$([1^2]^3) \otimes [1^3]' \# ([2]^2 \otimes [2]')$	10
M_9	$([1^2]^3) \otimes [3]' \# ([2]^2 \otimes [1^2]')$	10
W_4	$([1^2]^3) \otimes [21]' \# ([2]^2 \otimes [1^2]')$	20
M_{10}	$([1^2]^3) \otimes [1^3]' \# ([2]^2 \otimes [1^2]')$	10

Table III Character Table of the $S_5[S_2]$ group with 36 irreducible reps

	1^{10}	$1^8 2$	$1^6 2^2$	$1^4 2^3$	$1^2 2^4$	2^5	$1^6 2$	$1^6 4$	$1^4 2^3$	$1^4 2 4$	$1^2 2^4$	$1^2 2^2 4$	2^5	$2^3 4$	$1^4 3^2$	$1^4 6$	$1^2 2 3^2$	$1^2 2 6$
	1	5	10	10	5	1	20	20	60	60	60	60	20	20	80	80	160	160
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
A_3	1	-1	1	-1	1	-1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
A_4	1	-1	1	-1	1	-1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1
G_1	4	4	4	4	4	4	2	2	2	2	2	2	2	2	1	1	1	1
H_1	5	5	5	5	5	5	1	1	1	1	1	1	1	1	-1	-1	-1	-1
I_1	6	6	6	6	6	6	0	0	0	0	0	0	0	0	0	0	0	0
H_2	5	5	5	5	5	5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
G_2	4	4	4	4	4	4	-2	-2	-2	-2	-2	-2	-2	-2	1	1	1	1
G_3	4	-4	4	-4	4	-4	2	-2	-2	2	2	-2	-2	2	1	-1	-1	1
H_3	5	-5	5	-5	5	-5	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1
I_2	6	-6	6	-6	6	-6	0	0	0	0	0	0	0	0	0	0	0	0
H_4	5	-5	5	-5	5	-5	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1
G_4	4	-4	4	-4	4	-4	-2	2	2	-2	-2	2	2	-2	1	-1	-1	1
H_5	5	3	1	-1	-3	-5	3	3	1	1	-1	-1	-3	-3	2	2	0	0
R_1	15	9	3	-3	-9	-15	3	3	1	1	-1	-1	-3	-3	0	0	0	0
M_1	10	6	2	-2	-6	-10	0	0	0	0	0	0	0	0	-2	-2	0	0
R_2	15	9	3	-3	-9	-15	-3	-3	-1	-1	1	1	3	3	0	0	0	0
H_6	5	3	1	-1	-3	-5	-3	-3	-1	-1	1	1	3	3	2	2	0	0
H_7	5	-3	1	1	-3	5	3	-3	-1	1	-1	1	3	-3	2	-2	0	0
R_3	15	-9	3	3	-9	15	3	-3	-1	1	-1	1	3	-3	0	0	0	0
M_2	10	-6	2	2	-6	10	0	0	0	0	0	0	0	0	-2	2	0	0
R_4	15	-9	3	3	-9	15	-3	3	1	-1	1	-1	-3	3	0	0	0	0
H_8	5	-3	1	1	-3	5	-3	3	1	-1	1	-1	-3	3	2	-2	0	0

	$3^2 2^2$	$2^2 6$	$1^2 2^4$	2^5	$1^2 2^2 4$	$2^3 4$	$1^2 4^2$	24^2	$1^2 4^2$	$1^2 8$	24^2	$2 \ 8$	$2^2 3^2$	$2^2 6$	$4 \ 3^2$	$4 \ 6$	5^2	10
	80	80	60	60	120	120	60	60	240	240	240	240	160	160	160	160	384	384
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1
A_3	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	1	-1	-1	1	1	-1
A_4	1	-1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	1	-1
G_1	1	1	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1
H_1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	1	1	1	1	0	0
I_1	0	0	-2	-2	-2	-2	-2	-2	0	0	0	0	0	0	0	0	1	1
H_2	-1	-1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	0	0
G_2	1	1	0	0	0	0	0	0	0	0	0	0	1	1	1	1	-1	-1
G_3	1	-1	0	0	0	0	0	0	0	0	0	0	-1	1	1	-1	-1	1
H_3	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1	0	0
I_2	0	0	-2	2	2	-2	-2	2	0	0	0	0	0	0	0	0	1	-1
H_4	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1	0	0
G_4	1	-1	0	0	0	0	0	0	0	0	0	0	1	-1	-1	1	-1	1
H_5	-2	-2	1	-1	1	-1	1	-1	1	1	-1	-1	0	0	0	0	0	0
R_1	0	0	-1	1	-1	1	-1	1	-1	-1	1	1	0	0	0	0	0	0
M_1	2	2	2	-2	2	-2	2	-2	0	0	0	0	0	0	0	0	0	0
R_2	0	0	-1	1	-1	1	-1	1	1	1	-1	-1	0	0	0	0	0	0
H_6	-2	-2	1	-1	1	-1	1	-1	-1	-1	1	1	0	0	0	0	0	0
H_7	-2	2	1	1	-1	-1	1	1	1	-1	1	-1	0	0	0	0	0	0
R_3	0	0	-1	-1	1	1	-1	-1	-1	1	-1	1	0	0	0	0	0	0
M_2	2	-2	2	2	-2	-2	2	2	0	0	0	0	0	0	0	0	0	0
R_4	0	0	-1	-1	1	1	-1	-1	1	-1	1	-1	0	0	0	0	0	0
H_8	-2	2	1	1	-1	-1	1	1	-1	1	1	-1	0	0	0	0	0	0

	1^{10}	$1^8 2$	$1^6 2^2$	$1^4 2^3$	$1^2 2^4$	2^5	$1^6 2^2$	$1^6 4$	$1^4 2^3$	$1^4 2 4$	$1^2 2^4$	$1^2 2^2 4$	2^5	$2^3 4$	$1^4 3^2$	$1^4 6$	$1^2 2 3^2$	$1^2 2 6$
	1	5	10	10	5	1	20	20	60	60	60	60	20	20	80	80	160	160
M_3	10	2	-2	-2	2	10	4	2	0	-2	0	-2	4	2	1	1	-1	-1
W_1	20	4	-4	-4	4	20	2	-2	2	-2	2	-2	2	-2	-1	-1	1	1
M_4	10	2	-2	-2	2	10	-2	-4	2	0	2	0	-2	-4	1	1	-1	-1
M_5	10	2	-2	-2	2	10	2	4	-2	0	-2	0	2	4	1	1	-1	-1
W_2	20	4	-4	-4	4	20	-2	2	-2	2	-2	2	-2	2	-1	-1	1	1
M_6	10	2	-2	-2	2	10	-4	-2	0	2	0	2	-4	-2	1	1	-1	-1
M_7	10	-2	-2	2	2	-10	4	-2	0	-2	0	2	-4	2	1	-1	1	-1
W_3	20	-4	-4	4	4	-20	2	2	-2	-2	2	2	-2	-2	-1	1	-1	1
M_8	10	-2	-2	2	2	-10	-2	4	-2	0	2	0	2	-4	1	-1	1	-1
M_9	10	-2	-2	2	2	-10	2	-4	2	0	-2	0	-2	4	1	-1	1	-1
W_4	20	-4	-4	4	4	-20	-2	-2	2	2	-2	-2	2	2	-1	1	-1	1
M_{10}	10	-2	-2	2	2	-10	-4	2	0	2	0	-2	4	-2	1	-1	1	-1

	$3^2 2^2$	$2^2 6$	$1^2 2^4$	2^5	$1^2 2^2 4$	$2^3 4$	$1^2 4^2$	$2 4^2$	$1^2 4^2$	$1^2 8$	$2 4^2$	$2 8$	$2^2 3^2$	$2^2 6$	$4 3^2$	$4 6$	5^2	10
	80	80	60	60	120	120	60	60	240	240	240	240	160	160	160	160	384	384
M_3	1	1	2	2	0	0	-2	-2	0	0	0	0	1	1	-1	-1	0	0
W_1	-1	-1	0	0	0	0	0	0	0	0	0	0	-1	-1	1	1	0	0
M_4	1	1	-2	-2	0	0	2	2	0	0	0	0	1	1	-1	-1	0	0
M_5	1	1	-2	-2	0	0	2	2	0	0	0	0	-1	-1	1	1	0	0
W_2	-1	-1	0	0	0	0	0	0	0	0	0	0	1	1	-1	-1	0	0
M_6	1	1	2	2	0	0	-2	-2	0	0	0	0	-1	-1	1	1	0	0
M_7	1	-1	2	-2	0	0	-2	2	0	0	0	0	1	-1	1	-1	0	0
W_3	-1	1	0	0	0	0	0	0	0	0	0	0	-1	1	-1	1	0	0
M_8	1	-1	-2	2	0	0	2	-2	0	0	0	0	1	-1	1	-1	0	0
M_9	1	-1	-2	2	0	0	2	-2	0	0	0	0	-1	1	-1	1	0	0
W_4	-1	1	0	0	0	0	0	0	0	0	0	0	1	-1	1	-1	0	0
M_{10}	1	-1	2	-2	0	0	-2	2	0	0	0	0	-1	1	-1	1	0	0

Table IV Tunneling splittings of rotational levels to the semi-rigid to fully non-rigid (H₂O)₅

K	Semi-rigid (C _{5h})	Non-rigid (S ₅ [S ₂])
0	A ₁	A ₁ +A ₂ +A ₃ +A ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ + 2I ₁ +2I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ + 4W ₄
1	A ₁ + E ₁	(A ₁ +A ₂ +A ₃ +A ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ +2I ₁ + 2I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ +4W ₄)+ (G ₁ +G ₂ +G ₃ +G ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ + I ₁ +I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ + 4W ₄)
2	A ₁ +E ₁ +E ₂	(A ₁ +A ₂ +A ₃ +A ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ +2I ₁ + 2I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ +4W ₄)+ 2(G ₁ +G ₂ +G ₃ +G ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ + I ₁ +I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ + 4W ₄)
3	A ₁ +E ₁ +2E ₂	(A ₁ +A ₂ +A ₃ +A ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ +2I ₁ + 2I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ +4W ₄)+ 3(G ₁ +G ₂ +G ₃ +G ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ + I ₁ +I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ + 4W ₄)
4	A ₁ +2E ₁ +2E ₂	(A ₁ +A ₂ +A ₃ +A ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ +2I ₁ + 2I ₂ +2M ₁ +2M ₂ +2M ₃ +2M ₄ +2M ₅ +2M ₆ +2M ₇ +2M ₈ +2M ₉ +2M ₁₀ +3R ₁ +3R ₂ +3R ₃ +3R ₄ +4W ₁ + 4W ₂ + 4W ₃ +4W ₄)+ 4(G ₁ +G ₂ +G ₃ +G ₄ +H ₁ +H ₂ +H ₃ +H ₄ +H ₅ +H ₆ +H ₇ +H ₈ + I ₁

		$+I_2+2M_1+2M_2+2M_3+2M_4+2M_5+2M_6+2M_7+2M_8+2M_9$ $+2M_{10} +3R_1+3R_2+3R_3+3R_4+4W_1+ 4W_2+ 4W_3+ 4W_4)$
5	$2A_1+2E_1+2E_2$	$2(A_1+A_2+A_3+A_4+H_1+H_2+H_3+H_4+H_5+H_6+H_7+H_8+2I_1+$ $2I_2+2M_1+2M_2+2M_3+2M_4+2M_5+2M_6+2M_7+2M_8+2M_9$ $+2M_{10} +3R_1+3R_2+3R_3+3R_4+4W_1+ 4W_2+ 4W_3+4W_4)+$ $4(G_1+G_2+G_3+G_4+H_1+H_2+H_3+H_4+H_5+H_6+H_7+H_8+ I_1$ $+I_2+2M_1+2M_2+2M_3+2M_4+2M_5+2M_6+2M_7+2M_8+2M_9$ $+2M_{10} +3R_1+3R_2+3R_3+3R_4+4W_1+ 4W_2+ 4W_3+ 4W_4)$
n	$(A_1+2E_1+2E_2)+D^{n-5}$	$2(A_1+A_2+A_3+A_4+H_1+H_2+H_3+H_4+H_5+H_6+H_7+H_8+2I_1+$ $2I_2+2M_1+2M_2+2M_3+2M_4+2M_5+2M_6+2M_7+2M_8+2M_9$ $+2M_{10} +3R_1+3R_2+3R_3+3R_4+4W_1+ 4W_2+ 4W_3+4W_4)+$ $4(G_1+G_2+G_3+G_4+H_1+H_2+H_3+H_4+H_5+H_6+H_7+H_8+ I_1$ $+I_2+2M_1+2M_2+2M_3+2M_4+2M_5+2M_6+2M_7+2M_8+2M_9$ $+2M_{10} +3R_1+3R_2+3R_3+3R_4+4W_1+ 4W_2+ 4W_3+ 4W_4)$ D^{n-4}

Table V Proton and Deuterium Spin species of (H₂O)₅ and (D₂O)₅.

Sym	Proton Species	Deuterium Species	Sym	Proton Species	Deuterium
A ₁	³ A ₁ (1), ⁷ A ₁ (1), ¹¹ A ₁ (1)	¹ A ₁ (5) ⁵ A ₁ (7) ⁹ A ₁ (2) ¹¹ A ₁ (6) ¹³ A ₁ (2) ¹⁵ A ₁ (4) ¹⁷ A ₁ (1)	G ₃	None	³ G ₃ (1) ⁵ G ₃ (1) ⁷ G ₃ (1) ⁹ G ₃ (1)
A ₂	None	¹ A ₂ (1) ⁵ A ₂ (1)	H ₃	None	³ H ₃ (1) ⁵ H ₃ (1) ⁷ H ₃ (1)
A ₃	¹ A ₃	³ A ₃ (1), ⁷ A ₃ (1) ¹¹ A ₃ (1)	I ₂	None	¹ I ₂ (1) ⁵ I ₂ (1)
A ₄	None	None	H ₄	None	³ H ₄ (1)
G ₁	³ G ₁ ⁵ G ₁ ⁷ G ₁ ⁹ G ₁ ¹¹ G ₁	¹ G ₁ (4) ³ G ₁ (6) ⁵ G ₁ (12) ⁷ G ₁ (10) ⁹ G ₁ (11) ¹¹ G ₁ (7) ¹³ G ₁ (6) ¹⁵ G ₁ (3) ¹⁷ G ₁ (2) ¹⁹ G ₁ (1)	G ₄	None	None
H ₁	³ H ₁ ⁵ H ₁ ⁷ H ₁	¹ H ₁ (5) ³ H ₁ (5) ⁵ H ₁ (12) ⁷ H ₁ (9) ⁹ H ₁ (11) ¹¹ H ₁ (6) ¹³ H ₁ (5) ¹⁵ H ₁ (2) ¹⁷ H ₁ (1)	H ₅	¹ H ₅ (1) ⁵ H ₅ (1) ⁹ H ₅ (1)	³ H ₅ (9) ⁵ H ₅ (6) ⁷ H ₅ (10) ⁹ H ₅ (6) ¹¹ H ₅ (7) ¹³ H ₅ (3) ¹⁵ H ₅ (3) ¹⁷ H ₅ (1) ¹⁹ H ₅ (1)
I ₁	¹ I ₁ ⁵ I ₁	³ I ₁ (10) ⁵ I ₁ (7) ⁷ I ₁ (12) ⁹ I ₁ (6) ¹¹ I ₁ (7) ¹³ I ₁ (2) ¹⁵ I ₁ (2)	R ₁	³ R ₁ , ⁵ R ₁ , ⁷ R ₁	¹ R ₁ (4) ³ R ₁ (13) ⁵ R ₁ (17) ⁷ R ₁ (18) ⁹ R ₁ (14) ¹¹ R ₁ (10) ¹³ R ₁ (6) ¹⁵ R ₁ (3) ¹⁷ R ₁ (1)
H ₂	³ H ₂	¹ H ₂ (3) ³ H ₂ (4) ⁵ H ₂ (8) ⁷ H ₂ (6) ⁹ H ₂ (6) ¹¹ H ₂ (3) ¹³ H ₂ (2)	M ₁	¹ M ₁ ⁵ M ₁	¹ M ₁ (1) ³ M ₁ (9) ⁵ M ₁ (8) ⁷ M ₁ (11) ⁹ M ₁ (7) ¹¹ M ₁ (6) ¹³ M ₁ (2) ¹⁵ M ₁ (1)
G ₂	None	³ G ₂ (4) ⁵ G ₂ (3) ⁷ G ₂ (4) ⁹ G ₂ (2) ¹¹ G ₂ (1)	R ₂	³ R ₂	¹ R ₂ (5) ³ R ₂ (8) ⁵ R ₂ (13) ⁷ R ₂ (10) ⁹ R ₂ (9) ¹¹ R ₂ (4) ¹³ R ₂ (2)

H ₆	None	¹ H ₆ (1) ³ H ₆ (2) ⁵ H ₆ (3) ⁷ H ₆ (2) ⁹ H ₆ (1)	M ₅	None	³ M ₅ (6) ⁵ M ₅ (4) ⁷ M ₅ (6) ⁹ M ₅ (3) ¹¹ M ₅ (3) ¹³ M ₅ (1) ¹⁵ M ₅ (1)
H ₇	³ H ₇	¹ H ₇ (2) ³ H ₇ (1) ⁵ H ₇ (4) ⁷ H ₇ (2) ⁹ H ₇ (3) ¹¹ H ₇ (1) ¹³ H ₇ (1)	W ₂	None	¹ W ₂ (2) ³ W ₂ (7) ⁵ W ₂ (8) ⁷ W ₂ (8) ⁹ W ₂ (5) ¹¹ W ₂ (3) ¹³ W ₂ (1)
R ₃	None	¹ R ₃ (1) ³ R ₃ (4) ⁵ R ₃ (4) ⁷ R ₃ (4) ⁹ R ₃ (2) ¹¹ R ₃ (1)	M ₆	None	¹ M ₆ (2) ³ M ₆ (2) ⁵ M ₆ (4) ⁷ M ₆ (2) ⁹ M ₆ (2)
M ₂	None	¹ M ₂ (2) ³ M ₂ (1) ⁵ M ₂ (3) ⁷ M ₂ (1) ⁹ M ₂ (1)	M ₇	¹ M ₇ ⁵ M ₇	³ M ₇ (7) ⁵ M ₇ (5) ⁷ M ₇ (8) ⁹ M ₇ (4) ¹¹ M ₇ (4) ¹³ M ₇ (1) ¹⁵ M ₇ (1)
R ₄	None	³ R ₄ (2) ⁵ R ₄ (1) ⁷ R ₄ (1)	W ₃	None	¹ W ₃ (2) ⁵ W ₃ (6) ⁷ W ₃ (7) ⁹ W ₃ (6) ¹¹ W ₃ (4) ¹³ W ₃ (2) ¹⁵ W ₃ (1)
H ₈	None	None	M ₈	None	¹ M ₈ (2) ⁵ M ₈ (2) ⁹ M ₈ (1)
M ₃	³ M ₃ ⁷ M ₃	¹ M ₃ (6) ³ M ₃ (4) ⁵ M ₃ (12) ⁷ M ₃ (7) ⁹ M ₃ (9) ¹¹ M ₃ (4) ¹³ M ₃ (4) ¹⁵ M ₃ (1) ¹⁷ M ₃ (1)	M ₉	³ M ₉	¹ M ₉ (2) ³ M ₉ (4) ⁵ M ₉ (6) ⁹ M ₉ (5) ¹¹ M ₉ (4) ¹³ M ₉ (2) ¹⁵ M ₉ (1)
W ₁	³ W ₁ ⁵ W ₁	¹ W ₁ (5) ³ W ₁ (10) ⁵ W ₁ (15) ⁷ W ₁ (13) ⁹ W ₁ (11) ¹¹ W ₁ (6) ¹³ W ₁ (3) ¹⁵ W ₁ (1)	W ₄	None	¹ W ₄ (2) ³ W ₄ (5) ⁵ W ₄ (6) ⁷ W ₄ (5) ⁹ W ₄ (3) ¹¹ W ₄ (1)
M ₄	¹ M ₄	³ M ₄ (6) ⁵ M ₄ (4) ⁷ M ₄ (6) ⁹ M ₄ (2) ¹¹ M ₄ (2)	M ₁₀	None	³ M ₁₀ (1) ⁵ M ₁₀ (1) ⁷ M ₁₀ (1)

Table VI Nuclear Spin Statistical Weights of (H₂O)₅ (²H, ³D)

Symmetry	Nuclear Spin Statistical Weights (H) ^a	Nuclear Spin Weights (Deuterated) ^b	Symmetry	Nuclear Spin Statistical Weights (H) ^a	Nuclear Spin Weights (Deuterated) ^b
A ₁	1	252	R ₁	0	630
A ₂	0	6	M ₁	0	315
A ₃	21	21	R ₂	0	315
A ₄	0	0	H ₆	0	45
G ₁	0	504	H ₇	15	90
H ₁	0	420	R ₃	15	90
I ₁	0	336	M ₂	6	36
H ₂	0	210	R ₄	3	18
G ₂	0	84	H ₈	0	0
G ₃	24	24	M ₃	6	336
H ₃	15	15	W ₁	0	420
I ₂	6	6	M ₄	0	120
H ₄	3	3	M ₅	3	168
G ₄	0	0	W ₂	0	210
H ₅	3	378	M ₆	0	60
Sym	Stat (H)	Stat(D)	Sym	Stat (H)	Stat(D)
M ₇	10	210	M ₉	0	150
W ₃	8	168	W ₄	0	120
M ₈	1	21	M ₁₀	0	15

^asum of (stat weights x dimension of reps)=2¹⁰

^asum of (stat weights x dimension of reps)=3¹⁰

Table VII Correlation of rovibronic levels semi-rigid (H₂O)₅ to fully non-rigid (H₂O)₅ with

Nuclear Spin Statistical Weights in parenthesis

Semi-Rigid(C _{5h})	Non-rigid(S ₅ [S ₂])
A ₁ (208)	A ₁ (1)+A ₂ (0) +A ₃ (21)+A ₄ (0)+ H ₁ (0)+H ₂ (0)+H ₃ (15)+H ₄ (3)+H ₅ (3)+H ₆ (0)+H ₇ (15)+H ₈ (0)+ 2I ₁ (0) +2I ₂ (6)+2M ₁ (0)+2M ₂ (6)+2M ₃ (6)+2M ₄ (0)+2M ₅ (3) +2M ₆ (0)+2M ₇ (10)+2M ₈ (1)+2M ₉ (0)+2M ₁₀ (0) +3R ₁ (0)+3R ₂ (0)+3R ₃ (15) +3R ₄ (3)+4W ₁ (0)+ 4W ₂ (0)+ 4W ₃ (8)+ 4W ₄ (0)
E ₁ (204)	G ₁ (0)+G ₂ (0)+G ₃ (24)+G ₄ (0)+H ₁ (0)+H ₂ (0)+H ₃ (15)+H ₄ (3)+H ₅ (3) +H ₆ (0)+H ₇ (15)+H ₈ (0)+ I ₁ (0)+I ₂ (6)+2M ₁ (0)+2M ₂ (6)+2M ₃ (6)+2M ₄ (0) +2M ₅ (3)+2M ₆ (0)+2M ₇ (10)+2M ₈ (1)+2M ₉ (0)+2M ₁₀ (0)+3R ₁ (0)+3R ₂ (0) +3R ₃ (15)+3R ₄ (3)+4W ₁ (0)+ 4W ₂ (0)+ 4W ₃ (8)+ 4W ₄ (0)
E ₂ (204)	G ₁ (0)+G ₂ (0)+G ₃ (24)+G ₄ (0)+H ₁ (0)+H ₂ (0)+H ₃ (15)+H ₄ (3)+H ₅ (3) +H ₆ (0)+H ₇ (15)+H ₈ (0)+ I ₁ (0) +I ₂ (6)+2M ₁ (0)+2M ₂ (6)+2M ₃ (6) +2M ₄ (0)+2M ₅ (3)+2M ₆ (0)+2M ₇ (10)+2M ₈ (1)+2M ₉ (0)+2M ₁₀ (0) +3R ₁ (0)+3R ₂ (0)+3R ₃ (15)+3R ₄ (3)+ 4W ₁ (0)+ 4W ₂ (0)+ 4W ₃ (8)+ 4W ₄ (0)